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INTEGRALS INVOLVING r_{12}

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BIPOLAR ANGLE AVERAGES AND TWO-CENTER, TWO-PARTICLE INTEGRALS INVOLVING r_{12} *

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ABSTRACT

The bipolar angle average of a two-center, two-particle function $f(r_{a1}, r_{b2}, r_{12};R)$ is $\langle f \rangle = (4\pi)^{-2} \iint f \, d\omega_{a1} \, d\omega_{b2}$. A bipolar angle average weight function L_o is derived from geometrical considerations such that $\langle f \rangle = \int_{r_{12}(\min)}^{r_{12}(\max)} f \, L_o \, dr_{12}$. The L_o is independent of f and has a different, although simple, functional form in each of 42 regions of r_{a1}-r_{b2}-r_{12} space. However, the $\langle f \rangle$ have different functional forms in only four regions of r_{a1}-r_{b2} space. The expressions which we derive for the bipolar angle average are surprisingly simple and general, requiring only the evaluation of integrals of the form $\int f \, r_{12} dr_{12}$ and $\int f \, r_{12}^2 dr_{12}$. The bipolar angle averages are very useful in the evaluation of two-center, two-particle integrals. Many of our relations are greatly simplified by the use of homogeneous coordinates.

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I. Introduction

In quantum and statistical mechanics, one frequently has need to evaluate either the bipolar angle average or the integral over all (two-particle) space of a two-particle, two-center function $f(r_{a1}, r_{b2}, r_{12}; R)$. Here, as shown in Fig. 1, R is the separation between the two centers a and b; r_{12} is the separation between the two particles 1 and 2; and r_{a1} and r_{b2} are the separations between the indicated center and particle. In a subsequent paper, more general functions will be considered which, in addition, explicitly involve the angles θ_{a1}, ϕ_{a1}, θ_{b2}, and ϕ_{b2}.

The <u>bipolar angle average</u> of f is defined as

$$\langle f \rangle = (4\pi)^{-2} \iint f \, d\omega_{a1} \, d\omega_{b2} \qquad (1)$$

Here the integrations are over all the solid angles ω_{a1} and ω_{b2} ($d\omega_{a1} = \sin\theta_{a1}\, d\theta_{a1}\, d\phi_{a1}$ and $d\omega_{b2} = \sin\theta_{b2}\, d\theta_{b2}\, d\phi_{b2}$) while r_{a1}, r_{b2}, and R are held fixed.

Dahler, Hirschfelder, and Thacher[1] defined a <u>bipolar angle average weight function</u> $L_o(r_{a1}/R, r_{b2}/R, r_{12}/R; R)$ such that

$$\langle f \rangle = \int_{r_{12}(\min)}^{r_{12}(\max)} f \, L_o \, dr_{12} \qquad (2)$$

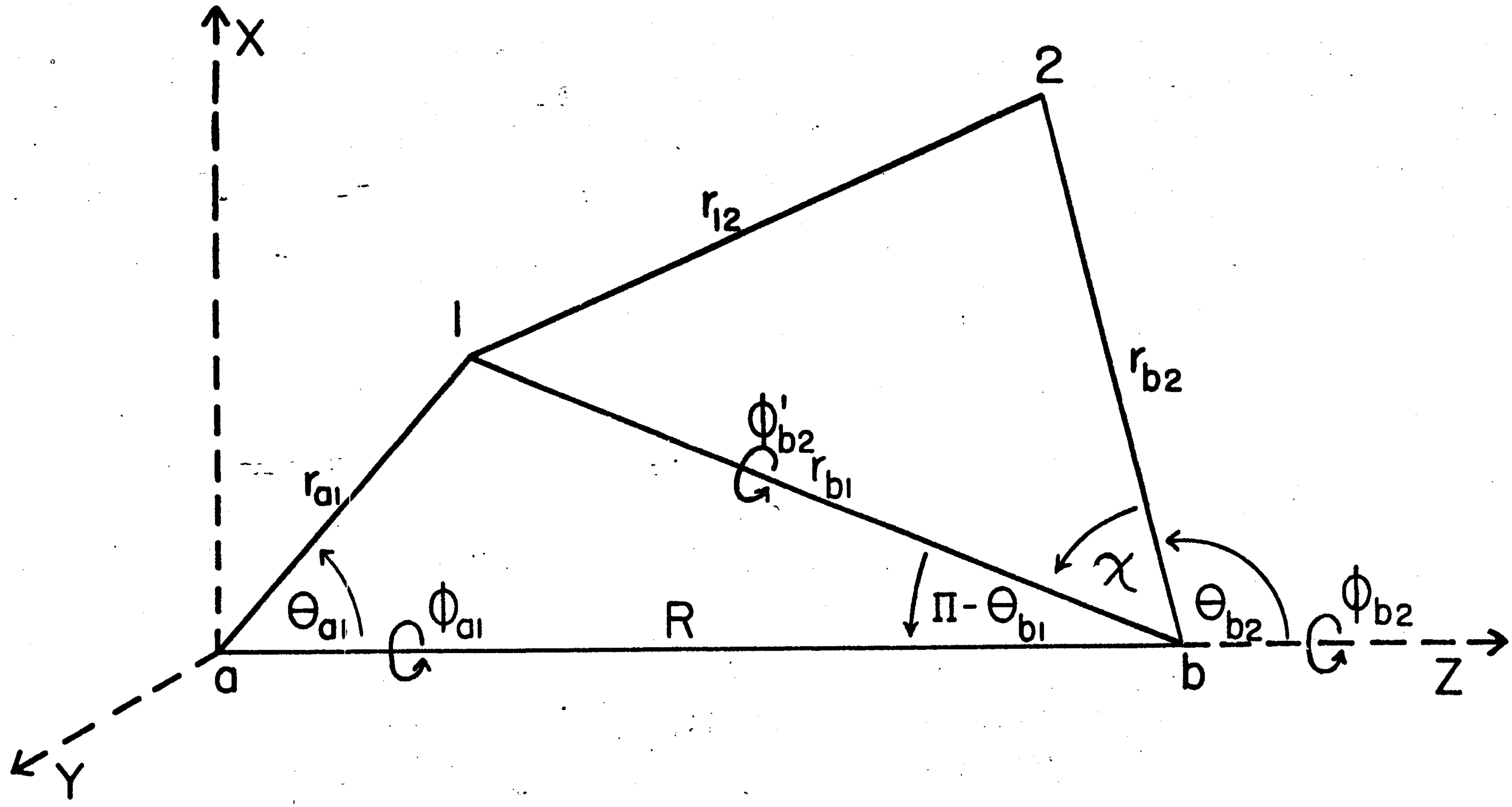

Fig. 1. Two-particle, Two-Center Coordinates

The weight function L_o is independent of the function f and can be determined from simple geometrical considerations. The derivation of L_o is given in Appendix A . For all values of r_{a1}/R , r_{b2}/R, and r_{12}/R the functional form of L_o is very simple. However, L_o has a different functional form in each of the 12 separate primary regions (determined by the ratios: r_{a1}/R and r_{b2}/R) shown in Fig. 2, and in each of the three or four secondary regions (determined by the ratio r_{12}/R) within each primary region. The critical distances and configurations within the primary regions which determine the secondary regions are shown in Fig. 3.

Table 1 gives the functional forms of L_o corresponding to the 21 secondary regions which comprise the half of two-particle configuration space for which $r_{a1} \leqslant r_{b2}$. In order to obtain the functional forms of L_o in the regions for which $r_{b2} \leqslant r_{a1}$, it is only necessary to interchange the roles of r_{a1} and r_{b2} . Dahler, Hirschfelder, and Thacher[1] determined L_o only for the "non-overlapping" primary region I_a and the "slightly overlapping" primary region IV_a , since only these regions were involved in their free-volume theory of liquids.

Considerable simplification of our expressions for the angle averages is achieved by using the homogeneous coordinates:

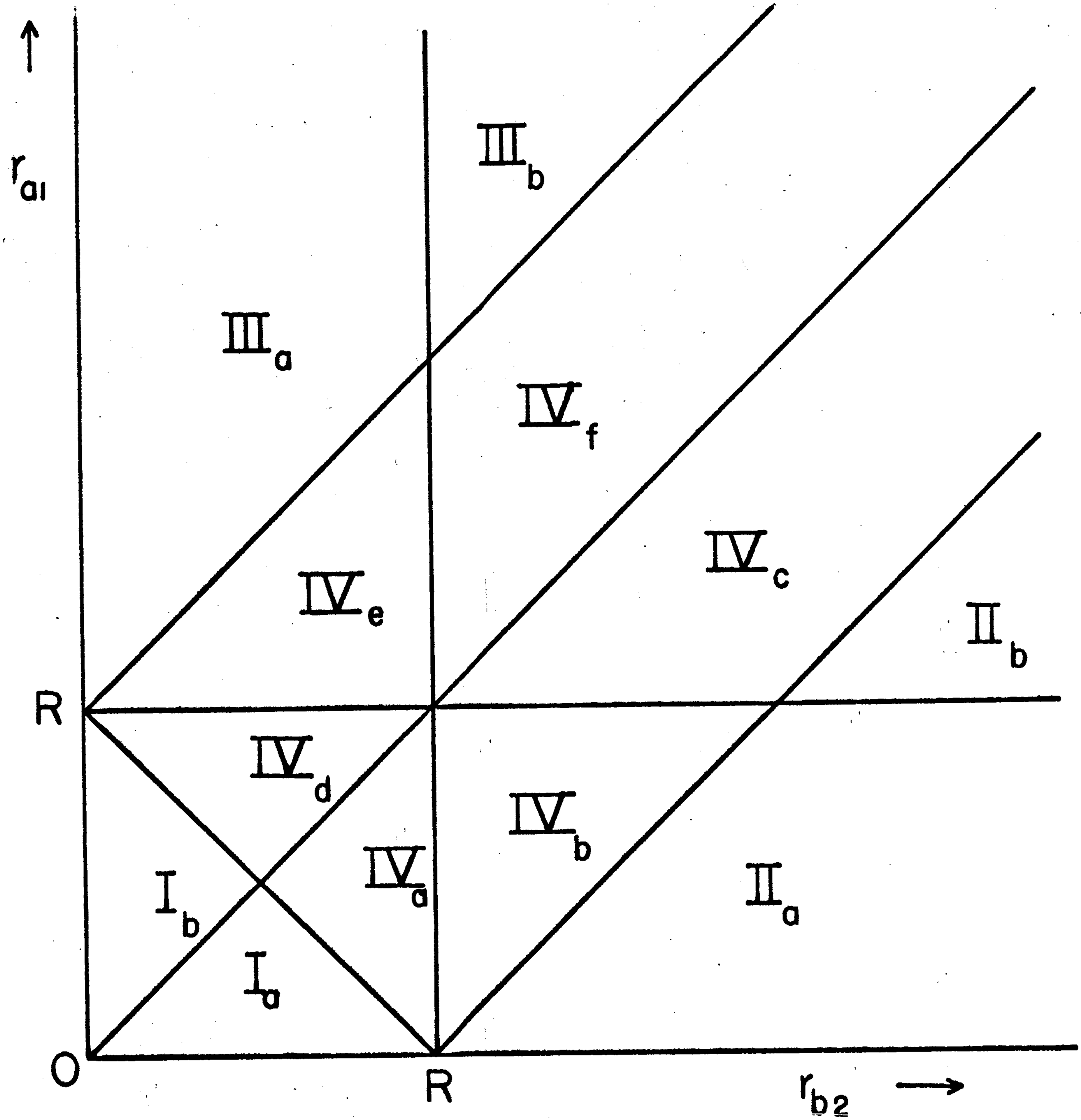

Fig. 2. Division of $r_{a1}-r_{b2}$ Plane into Twelve Primary Regions

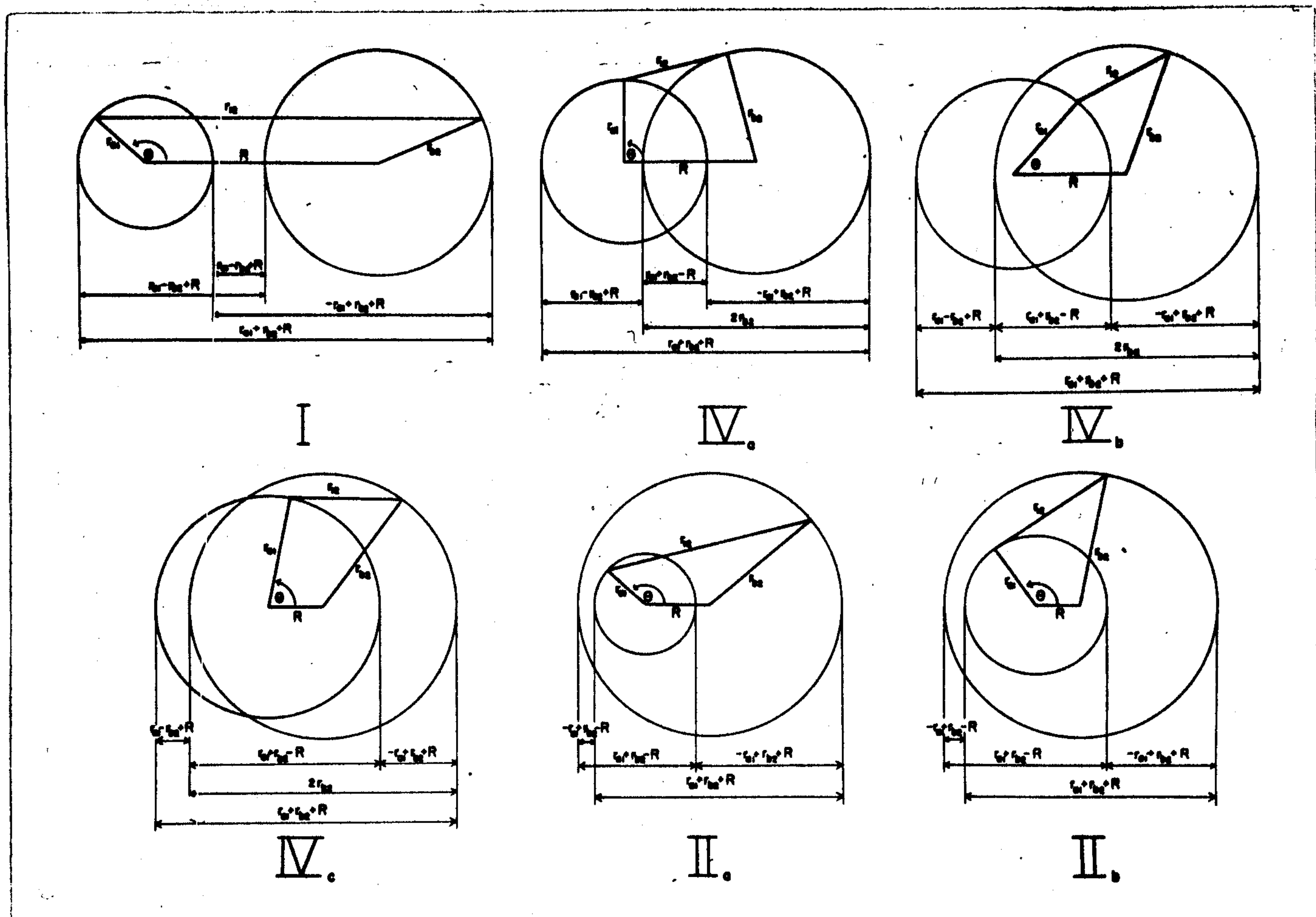

Fig. 3. Critical distances and configurations within primary regions which determine the secondary regions. The circles show why we call region I non-overlapping, IV$_a$ slightly overlapping, IV$_b$ and IV$_c$ greatly overlapping, and II enclosing.

Table 1

Functional form of L_o in each of the six primary regions (as shown in Fig. 2) for which $r_{a1} \leqslant r_{b2}$:

I_a : $r_{a1} + r_{b2} \leqslant R$, Non-overlapping

IV_a : $r_{b2} \leqslant R \leqslant r_{a1} + r_{b2}$, Slightly overlapping

IV_b : $r_{a1} \leqslant R$, $R \leqslant r_{b2} \leqslant R + r_{a1}$, Greatly overlapping

IV_c : $r_{a1} \geqslant R$, $R \leqslant r_{b2} \leqslant R + r_{a1}$, Greatly overlapping

II_a : $r_{a1} \leqslant R$, $R + r_{a1} \leqslant r_{b2}$, Enclosing

II_b : $r_{a1} \geqslant R$, $R + r_{a1} \leqslant r_{b2}$, Enclosing

The functional form of L_o in each of the other six regions is obtained by interchanging the role of r_{a1} and r_{b2} .

Primary Region	Secondary Region		$(4r_{a1}r_{b2}Rr_{12}^{-1})L_o$
I_a	(1)	$-u_3 \leqslant r_{12} \leqslant u_2$	$r_{12} + u_3$
	(2)	$u_2 \leqslant r_{12} \leqslant u_1$	$u_2 + u_3$
	(3)	$u_1 \leqslant r_{12} \leqslant u_o$	$-r_{12} + u_o$
IV_a	(1)	$0 \leqslant r_{12} \leqslant u_3$	$2r_{12}$
	(2)	$u_3 \leqslant r_{12} \leqslant u_2$	$r_{12} + u_3$
	(3)	$u_2 \leqslant r_{12} \leqslant u_1$	$u_2 + u_3$
	(4)	$u_1 \leqslant r_{12} \leqslant u_o$	$-r_{12} + u_o$

Table 1 (cont'd)

Primary Region		Secondary Region	$(4r_{a1}r_{b2}Rr_{12}^{-1})L_o$
IV_b	(1)	$0 \leq r_{12} \leq u_2$	$2r_{12}$
	(2)	$u_2 \leq r_{12} \leq u_3$	$r_{12} + u_2$
	(3)	$u_3 \leq r_{12} \leq u_1$	$u_2 + u_3$
	(4)	$u_1 \leq r_{12} \leq u_o$	$-r_{12} + u_o$
IV_c	(1)	$0 \leq r_{12} \leq u_2$	$2r_{12}$
	(2)	$u_2 \leq r_{12} \leq u_1$	$r_{12} + u_2$
	(3)	$u_1 \leq r_{12} \leq u_3$	$u_1 + u_2$
	(4)	$u_3 \leq r_{12} \leq u_o$	$-r_{12} + u_o$
II_a	(1)	$-u_2 \leq r_{12} \leq u_3$	$r_{12} + u_2$
	(2)	$u_3 \leq r_{12} \leq u_1$	$u_2 + u_3$
	(3)	$u_1 \leq r_{12} \leq u_o$	$-r_{12} + u_o$
II_b	(1)	$-u_2 \leq r_{12} \leq u_1$	$r_{12} + u_2$
	(2)	$u_1 \leq r_{12} \leq u_3$	$u_1 + u_2$
	(3)	$u_3 \leq r_{12} \leq u_o$	$-r_{12} + u_o$

$$
\begin{aligned}
u_o &= r_{a1} + r_{b2} + R \\
u_1 &= -r_{a1} + r_{b2} + R \\
u_2 &= r_{a1} - r_{b2} + R \\
u_3 &= r_{a1} + r_{b2} - R
\end{aligned}
\tag{3}
$$

Using the functional forms for L_o, as given in Table 1, it follows that in each of the 12 primary regions, $\langle f \rangle$ is the sum of three or four integrals (each corresponding to a secondary region). Quite surprisingly we found, by rearranging these integrals, that $\langle f \rangle$ has the same functional form in the primary regions I_a and I_b ; in II_a and II_b ; in III_a and III_b ; and again in IV_a , IV_b , IV_c , IV_d , and IV_e . Thus $\langle f \rangle$ has only four functional forms corresponding to the four master regions, as shown in Fig. 4 :

$$
\begin{aligned}
\mathrm{I} &: \quad r_{a1} + r_{b2} \leqslant R \\
\mathrm{II} &: \quad r_{b2} \geqslant r_{a1} + R \\
\mathrm{III} &: \quad r_{a1} \geqslant r_{b2} + R \\
\mathrm{IV} &: \quad |R - r_{a1}| \leqslant r_{b2} \leqslant r_{a1} + R
\end{aligned}
\tag{4}
$$

Letting a subscript indicate the master region, we obtain

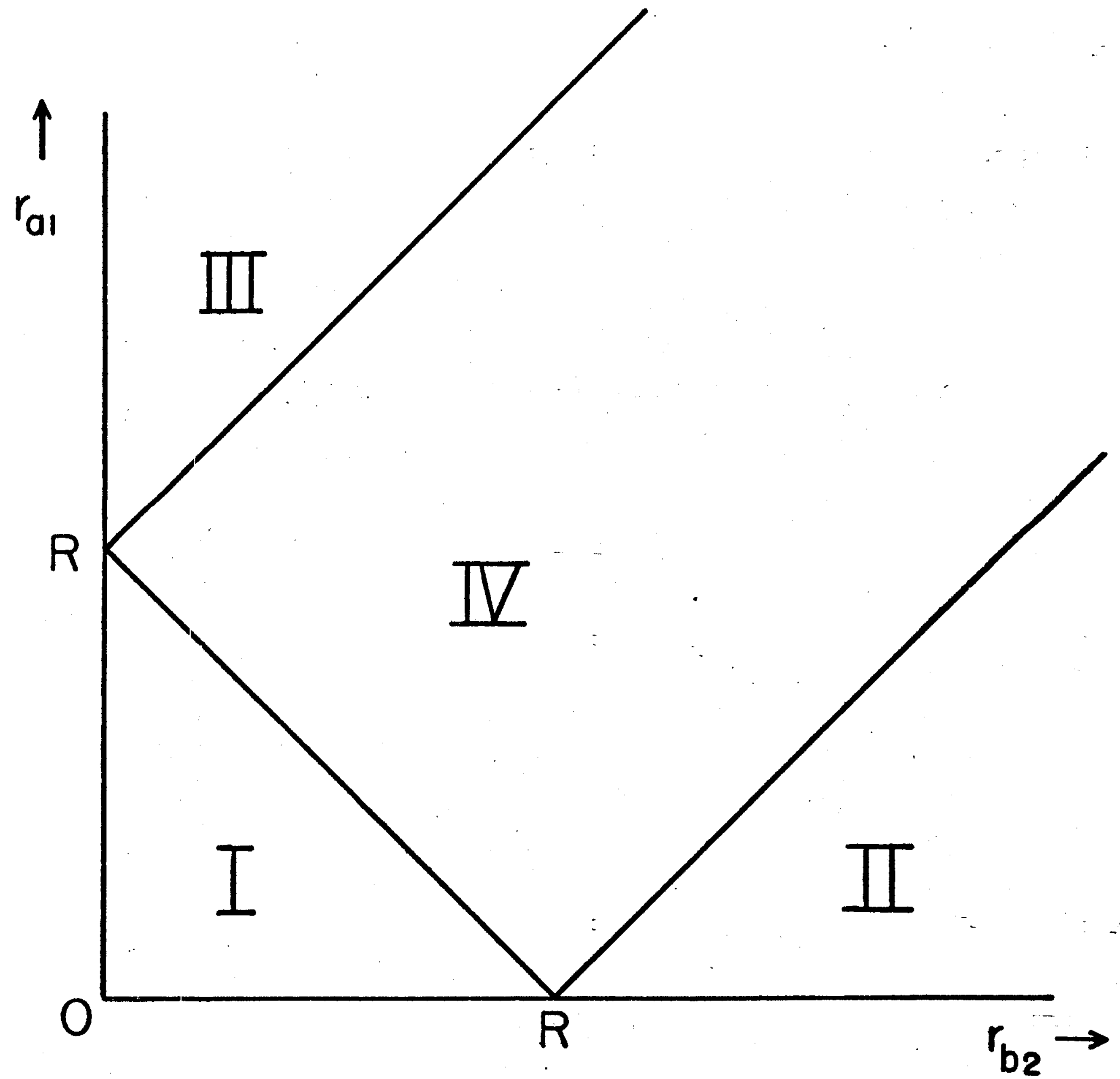

Fig. 4. Division of $r_{a1} - r_{b2}$ Plane into Four Master Regions.

$$\langle f \rangle_{I} = W(u_1) + W(u_2) - W(-u_3)$$

$$\langle f \rangle_{II} = W(u_1) - W(-u_2) + W(u_3)$$

$$\langle f \rangle_{III} = -W(-u_1) + W(u_2) + W(u_3) \tag{5}$$

$$\langle f \rangle_{IV} = W(u_1) + W(u_2) + W(u_3) - 2W(0)$$

Here the $W(x)$ are the r_{12} integrals which have only the one functional form:

$$W(x) = \frac{1}{4Rr_{a1}r_{b2}} \int_{x}^{u_o} (-r_{12} + x)r_{12}\, f\, (r_{a1}, r_{b2}, r_{12}; R)dr_{12} \tag{6}$$

Table 2 shows the signs of the u's in each of the master regions. The use of the homogeneous coordinates greatly simplifies our equations for the bipolar angle averages.

Table 2

Signs of the Homogeneous Coordinates in Each of the Master Regions

	Master Region I	II	III	IV
u_o	+	+	+	+
u_1	+	+	-	+
u_2	+	-	+	+
u_3	-	+	+	+

II. Bipolar Angle Average of Special Functions.

Let us consider the bipolar angle average of the following functional forms: $f = r_{12}^{\ n}$, $f = r_{12}^{\ -1} \exp(-\gamma\, r_{12})$, and $f = \delta(\underline{r}_1 - \underline{r}_2)$. From Eqs. (5) and (6) we obtain:

A. Bipolar Angle Average, $\langle r_{12}^{\ n} \rangle$

1. If n is <u>any</u> real number (integer or non-integer) except -2 or -3,

$$\langle r_{12}^{\ n} \rangle_{I} = (4(n+3)(n+2)R\ r_{a1}\ r_{b2})^{-1} \left[u_o^{\ n+3} - u_1^{\ n+3} - u_2^{\ n+3} + (-u_3)^{n+3} \right]$$

$$\langle r_{12}^{\ n} \rangle_{II} = (4(n+3)(n+2)R\ r_{a1}\ r_{b2})^{-1} \left[u_o^{\ n+3} - u_1^{\ n+3} + (-u_2)^{n+3} - u_3^{\ n+3} \right]$$

$$\langle r_{12}{}^{n}\rangle_{III} = (4(n+3)(n+2)R\ r_{a1}\ r_{b2})^{-1}\left[u_o{}^{n+3} + (-u_1)^{n+3} - u_2{}^{n+3} - u_3{}^{n+3}\right]$$

In master region IV, if $n \leq -3$, then $\langle r_{12}{}^{n}\rangle_{IV} = +\infty$.
However, if $n > -3$,

$$\langle r_{12}{}^{n}\rangle_{IV} = (4(n+3)(n+2)R\ r_{a1}\ r_{b2})^{-1}\left[u_o{}^{n+3} - u_1{}^{n+3} - u_2{}^{n+3} - u_3{}^{n+3}\right]$$

2. <u>$n = -1$.</u> Although this case is included in the general relations given above, it is sufficiently important to warrant explicit consideration.

$$\langle r_{12}{}^{-1}\rangle_{I} = \frac{1}{R}$$

$$\langle r_{12}{}^{-1}\rangle_{II} = \frac{1}{r_{b2}}$$

$$\langle r_{12}{}^{-1}\rangle_{III} = \frac{1}{r_{a1}}$$

$$\langle r_{12}{}^{-1}\rangle_{IV} = (4Rr_{a1}, r_{b2})^{-1}\left[-(r_{a1}-r_{b2})^2 + 2R(r_{a1} + r_{b2}) - R^2\right]$$

3. n = -2.

$$\langle r_{12}^{-2}\rangle_{I} = \langle r_{12}^{-2}\rangle_{II} = \langle r_{12}^{-2}\rangle_{III} = \langle r_{12}^{-2}\rangle_{IV}$$

$$= (4Rr_{a1}r_{b2})^{-1}\Big[u_o \ln|u_o| - u_1 \ln|u_1| - u_2 \ln|u_2| - u_3 \ln|u_3|\Big]$$

4. n = -3.

$$\langle r_{12}^{-3}\rangle_{I} = (4Rr_{a1}r_{b2})^{-1}\Big[\ln u_o + \ln u_1 + \ln u_2 - \ln|u_3|\Big]$$

$$\langle r_{12}^{-3}\rangle_{II} = (4R\, r_{a1}\, r_{b2})^{-1}\Big[-\ln u_o + \ln u_1 - \ln|u_2| + \ln u_3\Big]$$

$$\langle r_{12}^{-3}\rangle_{III} = (4R\, r_{a1}\, r_{b2})^{-1}\Big[-\ln u_o - \ln|u_1| + \ln u_2 + \ln u_3\Big]$$

$$\langle r_{12}^{-3}\rangle_{IV} = +\infty$$

It is easy to see why the $\langle r_{12}^{n}\rangle$ for even positive integer values of n are the same in all four master regions. Since

$$r_{12}^{2} = r_{a1}^{2} + r_{b2}^{2} + R^{2} - 2\, r_{a1}\, r_{b2}\Big[\cos\theta_{a1}\cos\theta_{b2} + \sin\theta_{a1}\sin\theta_{b2}(\phi_{a1}-\phi_{b2})\Big]$$

$$+ 2R\Big[r_{b2}\cos\theta_{b2} - r_{a1}\cos\theta_{a1}\Big],$$

it follows that r_{12}^2 can be expressed in terms of the normalized spherical harmonics (using the notation of MTGL[2]) :

$$r_{12}^2 = 4\pi \Big[(r_{a1}^2 + r_{b2}^2 + R^2)\, Y_0^0(\theta_{a1},\phi_{a1})\, Y_0^0(\theta_{b2},\phi_{b2})$$

$$- (2/3) r_{a1} r_{b2} \left[Y_1^0(\theta_{a1},\phi_{a1}) Y_1^0(\theta_{b2},\phi_{b2}) - Y_1^1(\theta_{a1},\phi_{a1}) Y_1^{-1}(\theta_{b2},\phi_{b2}) \right]$$

$$+ 2(3)^{-1/2} R \left[r_{b2}\, Y_0^0(\theta_{a1},\phi_{a1}) Y_1^0(\theta_{b2},\phi_{b2}) - r_{a1}\, Y_1^0(\theta_{a1},\phi_{a1}) Y_0^0(\theta_{b2},\phi_{b2}) \right] \Big] \tag{7}$$

By the addition theorems of spherical harmonics, it follows that any positive integer power of r_{12}^2 can also be expressed in terms of spherical harmonics, the same in all master regions. The $\langle r_{12}^n \rangle$ (for even positive integer values of n) is $(4\pi)^{-1}$ multiplied by the coefficient of $Y_0^0(\theta_{a1},\phi_{a1})\, Y_0^0(\theta_{b2}, \phi_{b2})$ in the spherical harmonic expansion of r_{12}^n.

B. Bipolar Angle Average, $\langle r_{12}^{-1} \exp(-\gamma\, r_{12}) \rangle$

Again using Eqs. (5) and (6), we obtain the bipolar angle average of the Yukawa potential in a simple form:

$$\left\langle \frac{1}{r_{12}} e^{-r_{12}} \right\rangle_{I} = (4Rr_{a1}r_{b2})^{-1}\gamma^{-2}\left[e^{-\gamma u_o} - e^{-\gamma u_1} - e^{-\gamma u_2} + e^{\gamma u_3}\right]$$

$$\left\langle \frac{1}{r_{12}} e^{-r_{12}} \right\rangle_{II} = (4Rr_{a1}r_{b2})^{-1}\gamma^{-2}\left[e^{-\gamma u_o} - e^{-\gamma u_1} + e^{\gamma u_2} - e^{-\gamma u_3}\right]$$

$$\left\langle \frac{1}{r_{12}} e^{-r_{12}} \right\rangle_{III} = (4Rr_{a1}r_{b2})^{-1}\gamma^{-2}\left[e^{-\gamma u_o} + e^{\gamma u_1} - e^{-\gamma u_2} - e^{-\gamma u_3}\right]$$

$$\left\langle \frac{1}{r_{12}} e^{-r_{12}} \right\rangle_{IV} = (4Rr_{a1}r_{b2})^{-1}\gamma^{-2}\left[e^{-\gamma u_o} - e^{-\gamma u_1} - e^{-\gamma u_2} - e^{-\gamma u_3} + 2\right]$$

C. Bipolar Angle Average of Three-Dimensional Delta Function, $\langle\delta(\underline{r}_1 - \underline{r}_2)\rangle$

The three dimensional delta function $\delta(\underline{r}_1 - \underline{r}_2)$ has the property that if $\psi(\underline{r}_2)$ is an arbitrary function of the coordinates of particle 2, then

$$\int \psi(\underline{r}_2)\,\delta(\underline{r}_1 - \underline{r}_2)\,d\tau = \psi(\underline{r}_1)\,. \tag{8}$$

Letting $\psi(\underline{r}_2) = 1$, it follows that

$$4\pi \int_0^\infty r_{12}^{\,2}\,\delta(\underline{r}_1 - \underline{r}_2)\,dr_{12} = 1\,. \tag{9}$$

Since $\delta(\underline{r}_1 - \underline{r}_2)$ is infinite when $r_{12} = 0$ and is otherwise zero, it is easy to see from Eqs. (5) and (6) that

$$\langle \delta(\underline{r}_1 - \underline{r}_2) \rangle_{I} = \langle \delta(\underline{r}_1 - \underline{r}_2) \rangle_{II} = \langle \delta(\underline{r}_1 - \underline{r}_2) \rangle_{III} = 0$$

$$\langle \delta(\underline{r}_1 - \underline{r}_2) \rangle_{IV} = (8\pi r_{a1} r_{b2} R)^{-1}$$

(10)

III. <u>Two-Center, Two-Particle Integrals</u>

By making use of the functional forms for the bipolar angle average, we obtain a method for evaluating two-particle, two-center integrals (over all space) of the form

$$I = \int\int f(r_{a1}, r_{b2}, r_{12}; R)\, d\tau_1\, d\tau_2 \qquad (11)$$

Thus,

$$\begin{aligned} I = {} & 16\pi^2 \int_0^R dr_{a1}\, r_{a1}^2 \Big[\int_0^{R-r_{a1}} dr_{b2}\, r_{b2}^2 \langle f \rangle_I \\ & + \int_{R-r_{a1}}^{R+r_{a1}} dr_{b2}\, r_{b2}^2 \langle f \rangle_{IV} + \int_{R+r_{a1}}^{\infty} dr_{b2}\, r_{b2}^2 \langle f \rangle_{II} \Big] \\ & + 16\pi^2 \int_R^{\infty} dr_{a1}\, r_{a1}^2 \Big[\int_0^{r_{a1}-R} dr_{b2}\, r_{b2}^2 \langle f \rangle_{III} \\ & + \int_{r_{a1}-R}^{r_{a1}+R} dr_{b2}\, r_{b2}^2 \langle f \rangle_{IV} + \int_{r_{a1}+R}^{\infty} dr_{b2}\, r_{b2}^2 \langle f \rangle_{II} \Big] \end{aligned}$$

(12)

Some previous procedures[3,4] for treating this type of integral are limited to integrands which factor into products of the type $f = q(r_{a1})\ s(r_{b2})\ t(r_{12})$ where q, s, and t have known Fourier transforms. In our treatment, $f(r_{a1}, r_{b2}, r_{12}; R)$ may be a completely general function, as our derivation only involves geometrical considerations.

In the limit as $R \to 0$, the integral I becomes a one-center, two-particle integral. As $R \to 0$, the master regions II and III cover the $r_{a1} - r_{b2}$ plane. Expanding $\langle f \rangle_{II}$ and $\langle f \rangle_{III}$, as given in Eq. (5), in Maclaurin series in powers of R and taking the limit as $R \to 0$, we obtain:

$$\langle f \rangle_{II} = (2\, r_{a1}\, r_{b2})^{-1} \int_{r_{b2} - r_{a1}}^{r_{a1} + r_{b2}} r_{12}\, f\, dr_{12}$$

$$\langle f \rangle_{III} = (2\, r_{a1}\, r_{b2})^{-1} \int_{r_{a1} - r_{b2}}^{r_{a1} + r_{b2}} r_{12}\, f\, dr_{12} \tag{5'}$$

Hence, Eq. (12) gives in the limit as $R \to 0$, since $r_{a1} = r_1$, $r_{b2} = r_2$, and I becomes a one-center, two-particle integral,

$$I = \int\int f \, d\tau_1 d\tau_2 = 8\pi^2 \int_0^\infty r_1 dr_1 \left\{ \int_{r_1}^\infty r_2 dr_2 \int_{r_2-r_1}^{r_1+r_2} r_{12} \, f \, dr_{12} + \int_0^{r_1} r_2 dr_2 \int_{r_1-r_2}^{r_1+r_2} r_{12} \, f \, dr_{12} \right\} \quad (13)$$

The same result can easily be found by direct integration.[5]

Making use of the bipolar angle average of $\delta(\underline{r}_1 - \underline{r}_2)$, Eq. (10), it is easy to reduce our Eq. (12) to correspond to the integration of a two-center, one-particle integral. First, let us take $f = g(r_{a1}, r_{b2}; R) \, \delta(\underline{r}_1 - \underline{r}_2)$. Then, from Eq. (8) it follows that Eq. (11) reduces to

$$I = \int g(r_{a1}, r_{b1}; R) \, d\tau_1 \qquad (14)$$

Now substituting the bipolar angle average of the delta function, Eq. (10), into Eq. (12):

$$\int g(r_{a1}, r_{b1}; R) \, d\tau_1 = 2\pi R^{-1} \int_0^R r_{a1} dr_{a1} \int_{R-r_{a1}}^{R+r_{a1}} g(r_{a1}, r_{b1}; R) r_{b1} dr_{b1} + 2\pi R^{-1} \int_R^\infty r_{a1} dr_{a1} \int_{r_{a1}-R}^{R+r_{a1}} g(r_{a1}, r_{b1}; R) r_{b1} dr_{b1} \qquad (15)$$

This same result may be obtained by direct integration[5]. (Express the integral in terms of ellipsoidal coordinates. Integrate over the angle ϕ. Then change variables from μ and λ to r_{a1} and r_{b2}.)

IV. Evaluation of a Sample Integral.

In order to illustrate the applicability of using the bipolar angle averages in the evaluation of two-center, two-particle integrals, we considered

$$K\,(n; \alpha, \beta; R) = \iint r_{12}^{n} \; a_1^{\,2}\, b_2^{\,2}\, d\tau_1 d\tau_2 \tag{16}$$

where

$$a_1 = \left(\frac{\alpha^3}{\pi}\right)^{1/2} e^{-\alpha r_{a1}}$$

and

$$b_2 = \left(\frac{\beta^3}{\pi}\right)^{1/2} e^{-\beta r_{b2}} \quad .$$

We restrict ourselves to integer values of $n \geqslant -2$. For half-integer values of n, the K integrals can probably be expressed in terms of the error function and its auxiliary functions.

Except for a few special cases, fractional values of n lead to K integrals which must be expressed in terms of difficult types of transcendental functions or infinite series. Using our relations for the $\langle r_{12} \rangle^n$ in the four master regions together with Eq. (12), we obtain rather easily the following results:

1. <u>$n = -1, 1, 3, \ldots$</u>

$K(n;\alpha, \beta ; R)$

$$= \sum_{k=1}^{1/2(n+3)} \sum_{j=1}^{1/2(n+5)-k} \frac{kj\;(n+1)!\; R^{n+4-2k-2j}}{(2\beta)^{2k-2}(2\alpha)^{2j-2}(n+5-2k-2j)!}$$

$$- \frac{(n+1)!\; e^{-2\alpha R}}{(2\alpha)^{n+1}} \left[\frac{\alpha\beta^4}{(\alpha^2-\beta^2)^2} + \frac{\beta^4\left[4\alpha^2+(n+3)(\alpha^2-\beta^2)\right]}{2(\alpha^2-\beta^2)^3}\,\frac{1}{R} \right]$$

$$- \frac{(n+1)!\; e^{-2\beta R}}{(2\beta)^{n+1}} \left[\frac{\beta\alpha^4}{(\beta^2-\alpha^2)^2} + \frac{\alpha^4\left[4\beta^2+(n+3)(\beta^2-\alpha^2)\right]}{2(\beta^2-\alpha^2)^3}\,\frac{1}{R} \right]$$

$K(n;\alpha,\alpha;R)$

$$= \sum_{k=0}^{1/2(n+3)} \sum_{j=0}^{1/2(n+5)-k} \frac{k\ j\ (n+1)!\ R^{n+4-2k-2j}}{(2\alpha)^{2k+2j-4}\ (n+5-2k-2j)!}$$

$$- \frac{(n+1)!\ e^{-2\alpha R}}{16(2\alpha)^{n-2}} \left[\frac{R^2}{3} + \frac{(n+4)R}{2\alpha} + \frac{(n+5)(n+4)-1}{4\alpha^2} + \frac{(n+7)(n+5)(n+3)}{24\alpha^3\ R} \right]$$

2. $\underline{n = 0,2,4,\ \ldots}$

$$K(n;\alpha,\beta;R) = \sum_{k=1}^{\frac{n}{2}+2} \sum_{j=1}^{\frac{n}{2}+2-k} \frac{kj(n+1)!\ R^{n+4-2k-2j}}{(2\beta)^{2k-2}(2\alpha)^{2j-2}\ (n+5-2k-2j)!}$$

3. $\underline{n = -2}$

$K(-2;\alpha,\beta;R)$

$$= \frac{\alpha^3\beta^3}{(\alpha^2-\beta^2)^2} \Bigg\{ \exp(+2\alpha R)\ Ei(-2\alpha R) \left[\frac{\beta}{\alpha} + \frac{\beta(\beta^2-5\alpha^2)}{2\alpha^2(\alpha^2-\beta^2)} \quad \frac{1}{R} \right]$$

$$+ \exp(-2\alpha R)\ Ei(+2\alpha R) \left[\frac{\beta}{\alpha} - \frac{\beta(\beta^2-5\alpha^2)}{2\alpha^2(\alpha^2-\beta^2)} \quad \frac{1}{R} \right] +$$

(continued on next page)

$$+ \exp(+2\beta R)\, Ei\,(-2\beta R)\left[\frac{\alpha}{\beta} + \frac{\alpha(\alpha^2 - 5\beta^2)}{2\beta^2(\beta^2 - \alpha^2)}\ \frac{1}{R}\right]$$

$$+ \exp\,(-2\beta R)\, Ei\,(+2\beta\, R)\left[\frac{\alpha}{\beta} - \frac{\alpha(\alpha^2 - 5\beta^2)}{2\beta^2(\beta^2 - \alpha^2)}\ \frac{1}{R}\right]\Bigg\}$$

where $Ei(x) = \int_{-\infty}^{x} y^{-1} \exp(\,y\,)\,dy$ and $Ei(\,-\,x) = -\int_{x}^{\infty} y^{-1} \exp(\,-y)dy.$

For $\alpha = \beta$ the integral simplifies considerably:

$K(-2;\alpha,\alpha\ ;\ R)$

$$= -\ \frac{7\alpha^2}{12} + \exp(+2\alpha R)Ei(-2\alpha R)\left[\frac{\alpha^4 R^2}{6} - \frac{\alpha^3 R}{2} + \frac{5\alpha^2}{8} - \frac{5\alpha}{16R}\right]$$

$$+ \exp(-2\alpha R)Ei(+2\alpha\, R)\left[\frac{\alpha^4 R^2}{6} + \frac{\alpha^3 R}{2} + \frac{5\alpha^2}{8} + \frac{5\alpha}{16R}\right]$$

For $n = 0$, we obtain $K(0;\alpha,\beta\ ;\ R\ ) = 1$, corresponding to the statement that the 1s "wave functions" a_1 and b_2 are normalized. For $n = -1$, the $K(-1;\alpha,\beta\ ;\ R\ )$ is the Coulombic integral which occurs in HeH^+ (for $\alpha \neq \beta$) and H_2 (for $\alpha = \beta$). Our expressions for this Coulombic integral agree with results given in quantum mechanical tables of integrals.

V. Discussion

In a subsequent paper, we shall consider bipolar angle averages of the form $\langle f\, Y^{m}_{j}(a1)\ Y^{-m}_{k}(b2)\rangle$ where the Y's are the normalized spherical harmonics involving θ_{a1}, ϕ_{a1} and θ_{b2}, ϕ_{b2} respectively and the f is a function of r_{a1}, r_{b2}, r_{12}, and R. If we know such bipolar angle averages for all values of j, k, and m, this is equivalent to knowing the bipolar expansion of f,

$$f = \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \sum_{m=-<}^{+<} (f\,|\,j,-m;k,m)\, Y^{-m}_{j}(a1)\ Y^{m}_{k}(b2) \tag{17}$$

Here the symbol $<$ indicates the lesser of j and k. Conversely, each coefficient $(f|j,-m;k,m)$ determines a bipolar angle average $< f\, Y^{m}_{j}(a1)\ Y^{-m}_{k}(b2) >$. Thus, $(f|0,0;0,0) = < f >$. In each of the four master regions, the $(f|j,-m;k,m)$ may be different functions of r_{a1}, r_{b2}, and R. For the function $f = r_{12}^{-1}$, Carlson and Rushbrooke[6] determined the set of coefficients in the master regions I, II, and III. Then Buehler and Hirschfelder[7,8] determined the $(r_{12}^{-1}|j,-m;k,m)$ in the difficult master region IV, as well as the coefficients in I, II, and III. Prigogine[9] obtained the expansion coefficients for $f = r_{12}^{-m}$ (where $m \geq 1$) in master region I. However, Prigogine's coefficients are in the form of infinite series which are not convenient to use. Subsequently, Sack[10] discovered a general relation for the expansion coefficients of $f = r_{12}^{n}$ in all four master regions for integer values of $n \geq -1$. Sack further claims that his relation is also valid for arbitrary values of n in master regions I, II, and III. For $n = -1$, his coefficients agree with those obtained by Carlson and Rushbrooke[6] and Buehler and Hirschfelder[7,8]. However, Sack's results are not convenient for integers $n < -1$ where his coefficients, expressed in powers of r_{a1}, r_{b2}, and R, are infinite series. Our coefficients, expressed in terms of the u_o, u_1, u_2, and u_3, are simple. In addition, Sack showed[11] that the expansion coefficients of the three dimensional delta function $\delta(\underline{r}_1 - \underline{r}_2)$ are only finite in master region IV. For a general function $f(r_{a1}, r_{b2}, r_{12}; R)$, Sack gives formulae for the expansion coefficients which correspond to expanding f in powers of r_{12}.

Sack's approach is quite different from ours. By considering the nature of the differential equations which are satisfied by the r_{12}^{n}, he established a recursion relation between the coefficients $(r_{12}^{n}|\ j,-m;k,m)$ and the coefficients $(r_{12}^{n-2}|\ j,-m;k,m)$. Furthermore, the coefficients of r_{12}^{n} may be expressed as the sum of terms of the form

$A_{n-s,s-t,t}\, r_{a1}^{\,n-s}\, r_{b2}^{\,s-t}\, R^{t}$, where s and t are integers. The allowed values of s and t are restricted by considering the required behaviour of $(r_{12}^{\,n}|j,-m;k,m)$ along the boundaries of the master region under consideration. From such studies, Sack determined the expansion coefficients in terms of the Appell functions F_4 (which are a generalization to two variables of the usual hypergeometric functions),

$$F_4(a,b;c,d;x,y) = \sum_{v}\sum_{w} \frac{(a;v+w)\ (b;v+w)\ x^{v}\ y^{w}}{(c;v)\ (d;w)\ v!\ w!} \tag{18}$$

Here the summation is over all non-negative integer values of v and w. We have used the notation:

$$\begin{aligned} (a;k) &= a(a+1)\ \ldots(a+k-1) \\ (a;0) &= 1 \qquad \text{and} \qquad (0;k) = \delta_{k0} \end{aligned} \tag{19}$$

Thus, for the coefficient $(r_{12}^{\,n}|0,0;0,0) = \langle r_{12}^{\,n}\rangle_{\text{Sack}}$ obtained in the four master regions[12] (indicated by the subscript):

$$\langle r_{12}^{\;n}\rangle_I = R^n F_4(-n/2, -(n+1)/2; 3/2, 3/2; r_{a1}^{\;2}/R^2, r_{b2}^{\;2}/R^2)$$

$$\langle r_{12}^{\;n}\rangle_{II} = r_{a1}^{\;n} F_4(-n/2, -(n+1)/2; 3/2, 3/2; R^2/r_{a1}^{\;2}, r_{b2}^{\;2}/R^2)$$

$$\langle r_{12}^{\;n}\rangle_{III} = r_{b2}^{\;n} F_4(-n/2. -(n+1)/2; 3/2, 3/2; R^2/r_{b2}^{\;2}, r_{a1}^{\;2}/r_{b2}^{\;2})$$

$$\langle r_{12}^{\;n}\rangle_{IV} = (1/2)\left[\langle r_{12}^{\;n}\rangle_I + \langle r_{12}^{\;n}\rangle_{II} + \langle r_{12}^{\;n}\rangle_{IV}\right]$$

$$-8\, r_{a1}^{\;-1} r_{b2}^{\;-1} R^{n+2} F_4\left((-1/2)(3+n),(-1/2)(2+n);1/2,1/2;\, r_{a1}^{\;2}/R^2, r_{b2}^{\;2}/R^2\right) .$$

(20)

It is clear that our relations in terms of the homogeneous coordinates are much simpler. Thus, from Sack's relations, given by Eq. (20), for the integer values of $n \geq -1$:

a) $n = -1, 1, 3, 5, \ldots$

$$\langle r_{12}^{\;n}\rangle_I = \sum_{\ell=0}^{1/2(n+1)} \sum_{j=0}^{1/2(n+1)-\ell} \frac{(n+1)!\, r_{a1}^{\;2j}\, r_{b2}^{\;2\ell}\, R^{n-2j-2\ell}}{(2j+1)!(2\ell+1)!\,(n-2j-2\ell)!}$$

$$\langle r_{12}^{\;n}\rangle_{II} = \sum_{\ell=0}^{(1/2)(n+1)} \sum_{j=0}^{(1/2)(n+1)-\ell} \frac{(n+1)!\, r_{a1}^{\;2j}\, r_{b2}^{\;2\ell-1}\, R^{(n-2\ell-2j)+1}}{(2j+1)!(2\ell)!\,\left[(n-2\ell-2j)+1\right]!}$$

$$\langle r_{12}{}^{n}\rangle_{III} = \sum_{\ell=0}^{(1/2)(n+1)} \sum_{j=0}^{(1/2)(n+1)-\ell} \frac{(n+1)!\; r_{a1}{}^{2j-1}\; r_{b2}{}^{2\ell}\; R^{(n-2\ell-2j)+1}}{(2j)!\;(2\ell+1)!\;\left[(n-2\ell-2j)+1\right]!}$$

$$\langle r_{12}{}^{n}\rangle_{IV} = \sum_{j=0}^{(1/2)(n+3)} \frac{-2(n+1)!}{(2j)!(n+3-2j)!} (r_{a1} - r_{b2})^{2j}\, R^{n+3-2j}$$

$$+\sum_{j=0}^{(1/2)(n+1)} \frac{2(n+1)!}{(2j)!\;(n+2-2j)!} (r_{a1} + r_{b2})^{2j+1}\, R^{n+2-2j}$$

b. $n = 0, 2, 4, \ldots$

$$\langle r_{12}{}^{n}\rangle_{I} = \langle r_{12}{}^{n}\rangle_{II} = \langle r_{12}{}^{n}\rangle_{III} = \langle r_{12}{}^{n}\rangle_{IV}$$

$$= \sum_{\ell=0}^{\frac{n}{2}} \sum_{j=0}^{\frac{n}{2}-\ell} \frac{(n+1)!\; r_{a1}{}^{2j}\; r_{b2}{}^{2\ell}\; R^{n-2j-2\ell}}{(2j+1)!\;(2\ell+1)!\;\left[(n-2j-2\ell)+1\right]!}$$

There are two reasons for giving so much attention to Sack's relations. First of all, expansions in powers of r_{a1}, r_{b2}, and R may be required for some uses of the bipolar angle averages. And, second, in our subsequent paper we will rely heavily on the work of Sack. Indeed, we shall need to refer to the above equations.

In our present paper, we derive a set of bipolar angle average weight functions which lead to a surprisingly simple and general relation for the bipolar angle average of a function $f(r_{a1},r_{b2},r_{12};R)$. These bipolar angle averages simplify the determination of two-center, two-particle integrals.

ACKNOWLEDGEMENTS

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APPENDIX A

Consider the two-center, two-particle bipolar angle average of a function $f(r_{a1}, r_{b2}, r_{12}; R)$. It is

$$\langle f \rangle = (4\pi)^{-2} \int d\omega_{a1} \int f(r_{a1}, r_{b2}, r_{12}; R)\, d\omega_{b2} \qquad \text{(A.1)}$$

where ω_{a1} and ω_{b2} are solid angles based on centers a and b , and the integration is carried out holding r_{a1}, r_{b2}, and R fixed. We can express $d\omega_{a1} = \sin\theta_{a1}\, d\theta_{a1}\, d\phi_{a1}$ with the polar axis pointed from a to b . For $d\omega_{b2}$ it is convenient to take the polar axis from b to a along the line b1. Thus, $d\omega_{b2} = \sin\chi d\chi d\phi'_{b2}$, where the angles χ and ϕ'_{b2} are shown in Fig. 1. Eq. (A.1) then becomes

$$\langle f \rangle = (4\pi)^{-2} \int_0^{\pi} \sin\theta_{a1} d\theta_{a1} \int_0^{2\pi} d\phi_{a1} \int_0^{\pi} \sin\chi d\chi \int_0^{2\pi} f\, d\phi'_{b2} \,. \qquad \text{(A.2)}$$

But r_{12} is independent of ϕ_{a1} and ϕ'_{b2} and therefore

$$\langle f \rangle = (1/4) \int_0^{\pi} \sin\theta_{a1} d\theta_{a1} \int_0^{\pi} f \sin\chi\, d\chi \quad . \qquad \text{(A.3)}$$

Now let us define a bipolar angle average weight function L_o such that

$$\langle f \rangle = \int_{r_{12}(\min)}^{r_{12}(\max)} f(r_{a1}, r_{b2}, r_{12}; R)\, L_o(r_{a1}, r_{b2}, r_{12}; R)\, dr_{12} \,. \tag{A.4}$$

At this point we pause to introduce useful notation. Two-dimensional representations of the two-particle, two-center system are drawn in Fig. 3. These consist of a circle "a" of radius r_{a1} about center a and a circle "b" of radius r_{b2} about center b. The r_{a1}, r_{b2}, r_{12}, R, and θ_{a1} are defined as before. If the circles intersect, the angle θ_{a1} measured to the point of intersection is denoted by θ_{int}.

First let us consider the regions IV_a, IV_b and IV_c where the spheres "a" and "b" intersect. In order to determine L_o, we first hold θ_{a1} constant and determine the area swept out on circle "b" which is characterized by the range r_{12} to $r_{12} + \delta r_{12}$. This area is shown in Fig. 5 (for a non-overlapping region). Then we integrate over θ_{a1}. Thus

$$L_o = \frac{1}{4}\left[\int_0^{\theta_{int}} \sin\theta_{a1}\, d\theta_{a1} \int_{\chi(r_{12})}^{\chi(r_{12}+\delta r_{12})} \sin\chi\, d\chi + \int_{\theta_{int}}^{\pi} \sin\theta_{a1}\, d\theta_{a1} \int_{\chi(r_{12})}^{\chi(r_{12}+\delta r_{12})} \sin\chi\, d\chi \right] \tag{A.5}$$

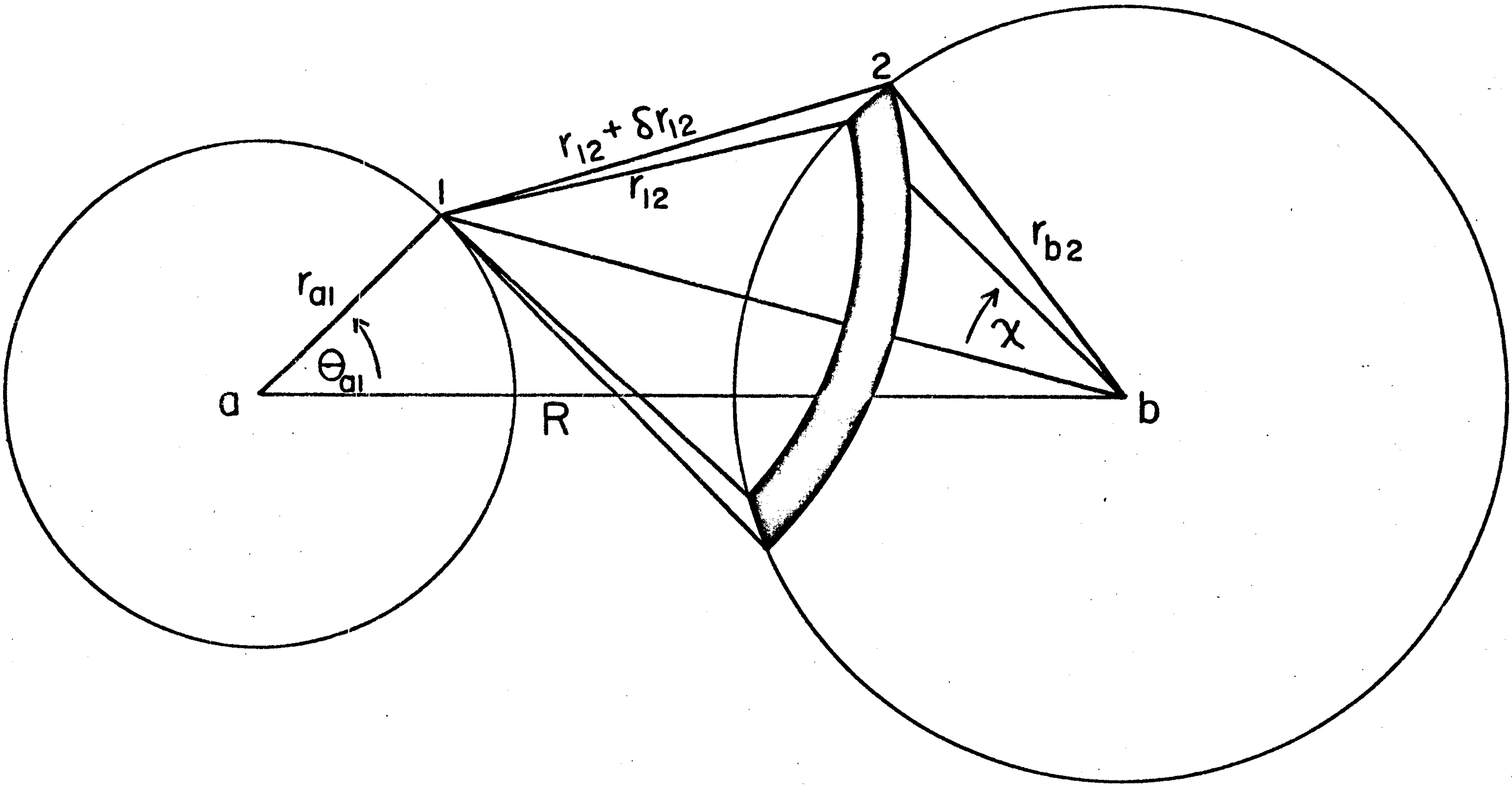

Fig. 5. Area swept out on circle "b" from a point on circle "a" with θ_{a1}, r_{a1}, r_{b2}, and R held constant and r_{12} lying in the range r_{12} to $r_{12}+\delta r_{12}$.

It is necessary to split the integral at θ_{int} because a particular value of r_{12} and χ may correspond to two angles θ_{a1} ; the one less than θ_{int} is called an interior angle and is denoted by the subscript "i"; the other, greater than θ_{int}, is called an exterior angle and is denoted by the subscript "e". In carrying out the integration of Eq. (A.5), we find that L_o has a simple functional form in each of a number of ranges of r_{12}. Each of these ranges is called a secondary region. Within a particular secondary region, θ_{a1} is required to lie either within the interval

$$\theta_{1i} \leq \theta_{a1} \leq \theta_{2i} \leq \theta_{int}$$

or within the interval

$$\theta_{int} \leq \theta_{1e} \leq \theta_{a1} \leq \theta_{2e} \quad .$$

Here the limiting angles θ_{1i} , θ_{2i} , θ_{1e} and θ_{2e} are determined by geometrical considerations as shown in Figs. 6 through 11. From Fig. 1. we have

$$\cos\chi = \frac{r_{a1}^{\;2} + r_{b2}^{\;2} + R^2 - r_{12}^{\;2} - 2Rr_{a1}\cos\theta_{a1}}{2r_{b2}(R^2 + r_{a1}^{\;2} - 2Rr_{a1}\cos\theta_{a1})^{1/2}} \tag{A.6}$$

from which

$$\sin\chi \, d\chi = \frac{r_{12} dr_{12}}{r_{b2}(R^2 + r_{a1}^{\;2} - 2Rr_{a1}\cos\theta_{a1})^{1/2}} . \tag{A.7}$$

Hence

$$L_o = \frac{r_{12}}{4Rr_{b2}} \left\{ \int_{\theta_{1i}}^{\theta_{2i}} \frac{\sin\theta_{a1} d\theta_{a1}}{(R^2 + r_{a1}^{\;2} - 2Rr_{a1}\cos\theta_{a1})^{1/2}} + \int_{\theta_{1e}}^{\theta_{2e}} \frac{\sin\theta_{a1} d\theta_{a1}}{(R^2 + r_{a1}^{\;2} - 2Rr_{a1}\cos\theta_{a1})^{1/2}} \right\} . \tag{A.8}$$

Now we immediately obtain,

$$L_o = \frac{r_{12}}{4Rr_{a1}r_{b2}} \left[(t_{2i} - t_{1i}) + (t_{2e} - t_{1e}) \right] \tag{A.9}$$

where

$$\begin{aligned} t_{1i} &= (R^2 + r_{a1}^{\;2} - 2Rr_{a1}\cos\theta_{1i})^{1/2} \\ t_{2i} &= (R^2 + r_{a1}^{\;2} - 2Rr_{a1}\cos\theta_{2i})^{1/2} \\ t_{1e} &= (R^2 + r_{a1}^{\;2} - 2Rr_{a1}\cos\theta_{1e})^{1/2} \end{aligned} \tag{A.10}$$

(continued on next page)

$$t_{2e} = (R^2 + r_{a1}{}^2 - 2Rr_{a1}\cos\theta_{2e})^{1/2} \quad .$$

These t's are listed in Table 3. The resulting values of L_o are then given in Table 1. If the angle θ_{a2} corresponding to a value of t is desired, it may be obtained from

$$\cos\theta_{a1} = \frac{R^2 + r_{a1}{}^2 - t^2}{2Rr_{a1}} \quad . \tag{A.11}$$

In region I_a, II_a and II_b where the spheres "a" and "b" do not intersect, the analysis is the same with the exception that θ_{int} is equal to 0 or to π, so that in Eq. (A.8) there is only one range of integration: either from θ_{1e} to θ_{2e} (in region I_a where $\theta_{int} = 0$); or from θ_{1i} to θ_{2i} (in regions II_a and II_b where $\theta_{int} = \pi$). Correspondingly, in Eq. (A.9), in region I_a, the $t_{1i} = t_{2i} = 0$ whereas in region II_a and II_b, the $t_{1e} = t_{2e} = 0$. The values of the t's are given in Table 3 and the corresponding L_o's are listed in Table 1.

Table 3

Values of t's in the Secondary Regions. The Figures used in their Evaluation are Indicated

Primary Region	Secondary Regions		Figures	t_{1e}	t_{2e}	t_{1i}	t_{2i}
I_a	(1)	$-u_3 \leqslant r_{12} \leqslant u_2$	(6.1) and (6.2)	$-r_{a1} + R$	$r_{12} + r_{b2}$	0	0
	(2)	$u_2 \leqslant r_{12} \leqslant u_1$	(6.3) and (6.4)	$-r_{a1} + R$	$r_{a1} + R$		
	(3)	$u_1 \leqslant r_{12} \leqslant u_o$	(6.5) and (6.6)	$r_{12} - r_{b2}$	$r_{a1} + R$		
II_a	(1)	$-u_2 \leqslant r_{12} \leqslant u_3$	(7.1) and (7.2)	0	0	$-r_{12} + r_{b2}$	$r_{a1} + R$
	(2)	$u_3 \leqslant r_{12} \leqslant u_1$	(7.3) and (7.4)	0	0	$-r_{a1} + R$	$r_{a1} + R$
	(3)	$u_1 \leqslant r_{12} \leqslant u_o$	(7.5) and (7.6)	0	0	$r_{12} - r_{b2}$	$r_{a1} + R$
II_b	(1)	$-u_2 \leqslant r_{12} \leqslant u_1$	(8.1) and (8.2)	0	0	$-r_{12} + r_{b2}$	$r_{a1} + R$
	(2)	$u_1 \leqslant r_{12} \leqslant u_3$	(8.3) and (8.4)	0	0	$r_{a1} - R$	$r_{a1} + R$
	(3)	$u_3 \leqslant r_{12} \leqslant u_o$	(8.5) and (8.6)	0	0	$r_{12} - r_{b2}$	$r_{a1} + R$
IV_a	(1) interior	$0 \leqslant r_{12} \leqslant u_3$	(9.1) and (9.2)	0	0	$-r_{12} + r_{b2}$	r_{b2}
	exterior	$0 \leqslant r_{12} \leqslant u_2$	(9.7) and (9.8)	r_{b2}	$r_{12} + r_{b2}$	0	0
	(2) interior	$u_3 \leqslant r_{12} \leqslant u_1$	(9.3) and (9.4)	0	0	$-r_{a1} + R$	r_{b2}
	exterior	$u_2 \leqslant r_{12} \leqslant 2r_{b2}$	(9.9) and (9.10)	r_{b2}	$r_{a1} + R$	0	0
	(3) interior	$u_1 \leqslant r_{12} \leqslant 2r_{b2}$	(9.5) and (9.6)	0	0	$r_{12} - r_{b2}$	r_{b2}
	exterior	$2r_{b2} \leqslant r_{12} \leqslant u_o$	(9.11) and (9.12)	$r_{12} - r_{b2}$	$r_{a1} + R$	0	0

(continued on next page)

Table 3 (cont'd)

Values of t's in the Secondary Regions. The Figures used in their Evaluation are Indicated

Primary Region	Secondary Regions	Figures	t_{1e}	t_{2e}	t_{1i}	t_{2i}
IV_b	(1) interior $0 \leq r_{12} \leq u_3$	(10.1) and (10.2)	0	0	$-r_{12} + r_{b2}$	r_{b2}
	exterior $0 \leq r_{12} \leq u_2$	(10.7) and (10.8)	r_{b2}	$r_{12} + r_{b2}$	0	0
	(2) interior $u_3 \leq r_{12} \leq u_1$	(10.3) and (10.4)	0	0	$-r_{a1} + R$	r_{b2}
	exterior $u_2 \leq r_{12} \leq 2r_{b2}$	(10.9) and (10.10)	r_{b2}	$r_{a1} + R$	0	0
	(3) interior $u_1 \leq r_{12} \leq 2r_{b2}$	(10.5) and (10.6)	0	0	$r_{12} - r_{b2}$	r_{b2}
	exterior $2r_{b2} \leq r_{12} \leq u_o$	(10.11) and (10.12)	$r_{12} - r_{b2}$	$r_{a1} + R$	0	0
IV_c	(1) interior $0 \leq r_{12} \leq u_1$	(11.1) and (11.2)	0	0	$-r_{12} + r_{b2}$	r_{b2}
	exterior $0 \leq r_{12} \leq u_2$	(11.7) and (11.8)	r_{b2}	$r_{12} + r_{b2}$	0	0
	(2) interior $u_1 \leq r_{12} \leq u_3$	(11.3) and (11.4)	0	0	$r_{a1} - R$	r_{b2}
	exterior $u_2 \leq r_{12} \leq 2r_{b2}$	(11.9) and (11.10)	r_{b2}	$r_{a1} + R$	0	0
	(3) interior $u_3 \leq r_{12} \leq 2r_{b2}$	(11.5) and (11.6)	0	0	$r_{12} - r_{b2}$	r_{b2}
	exterior $2r_{b2} \leq r_{12} \leq u_o$	(11.11) and (11.12)	$r_{12} - r_{b2}$	$r_{a1} + R$	0	0

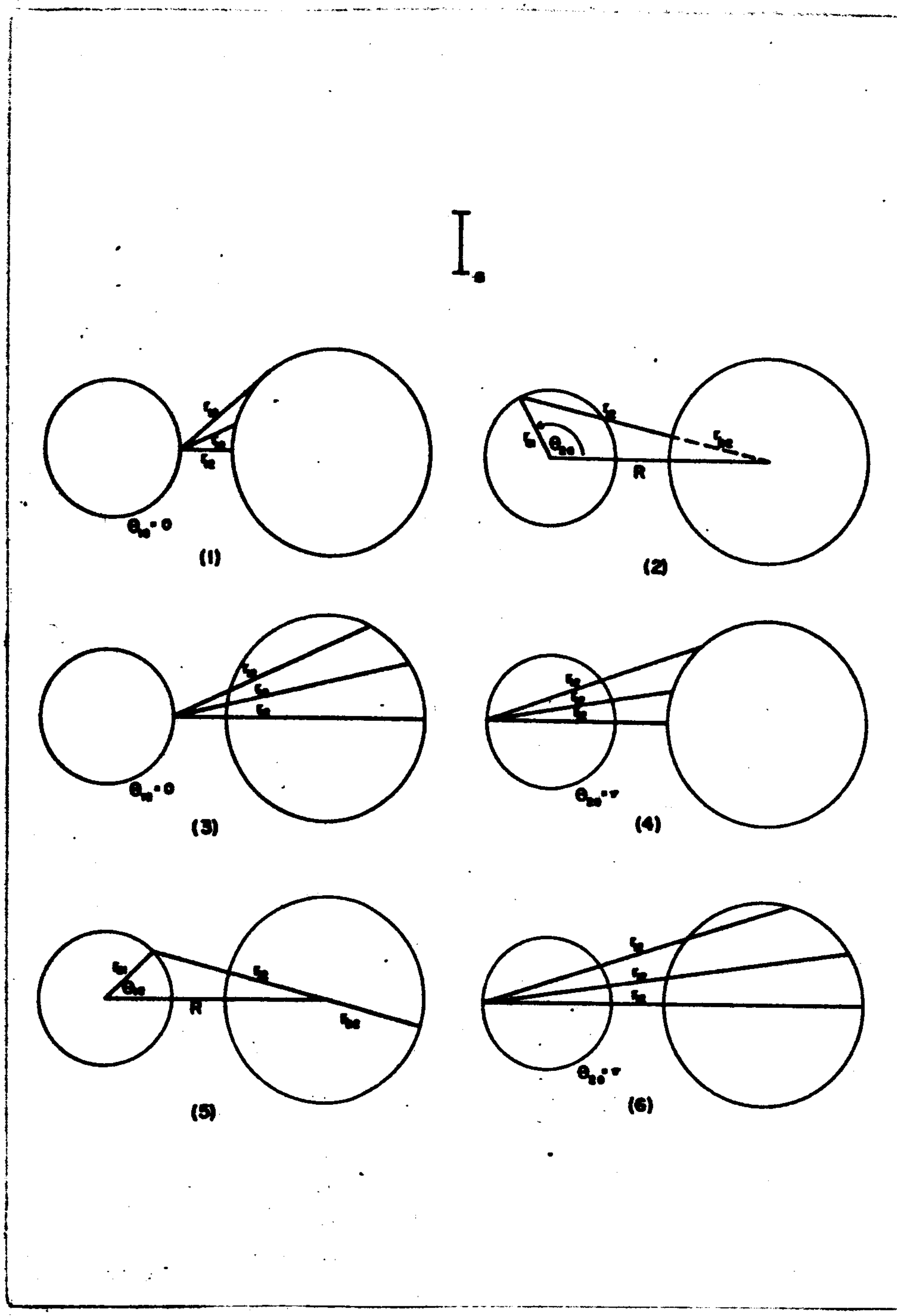

Fig. 6. The Limiting Angles θ_{1e} and θ_{2e} for Region I_a. Subfigures (1) and (2) refer to Secondary Region $I_a(1)$; (3) and (4) refer to $I_a(2)$; and (5) and (6) to $I_a(3)$.

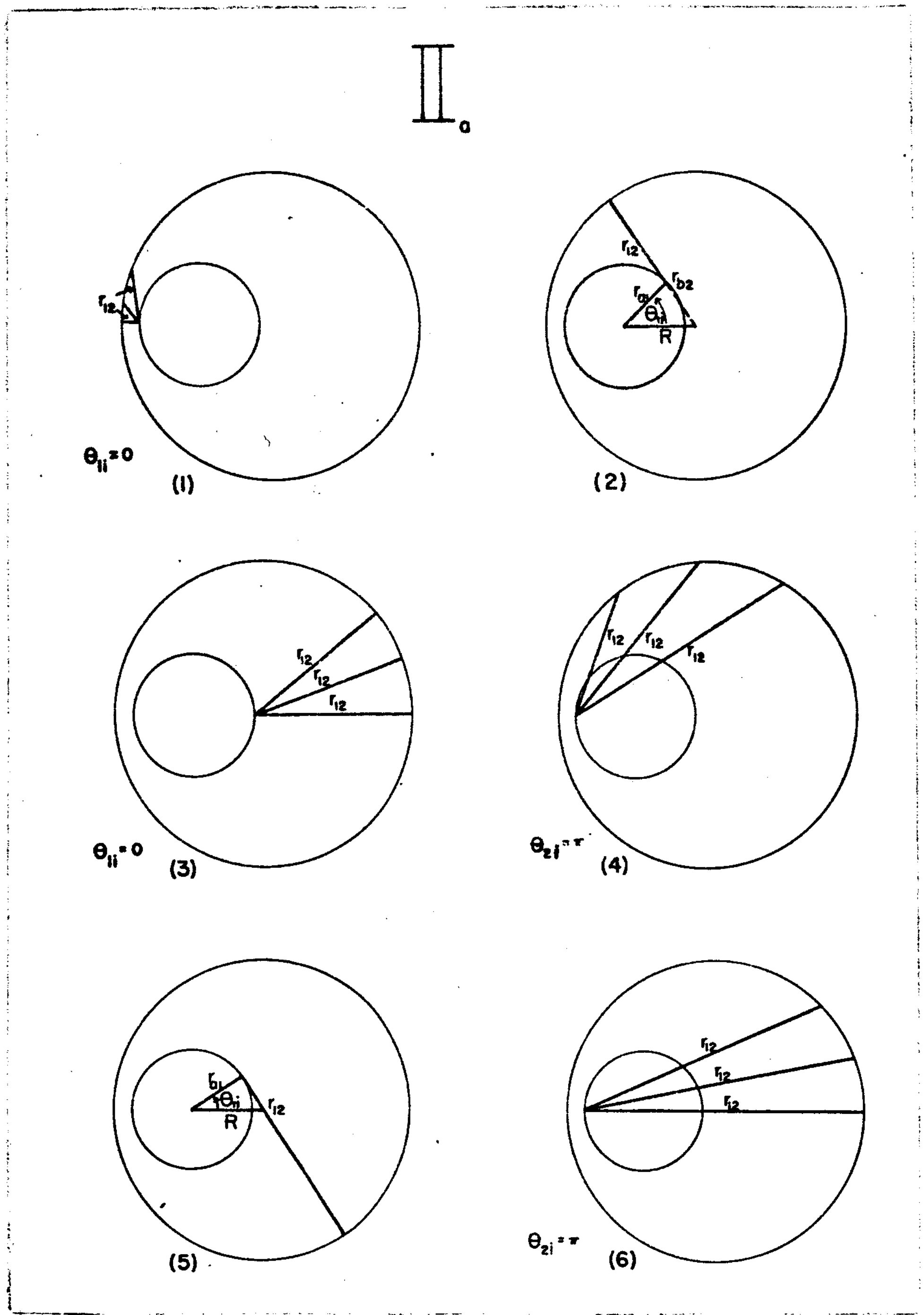

Fig. 7. The Limiting Angles θ_{1i} and θ_{2i} for Region II_a. Subfigures (1) and (2) refer to the Secondary Region II_a (1); (3) and (4) refer to II_a(2); and (5) and (6) refer to II_a(3).

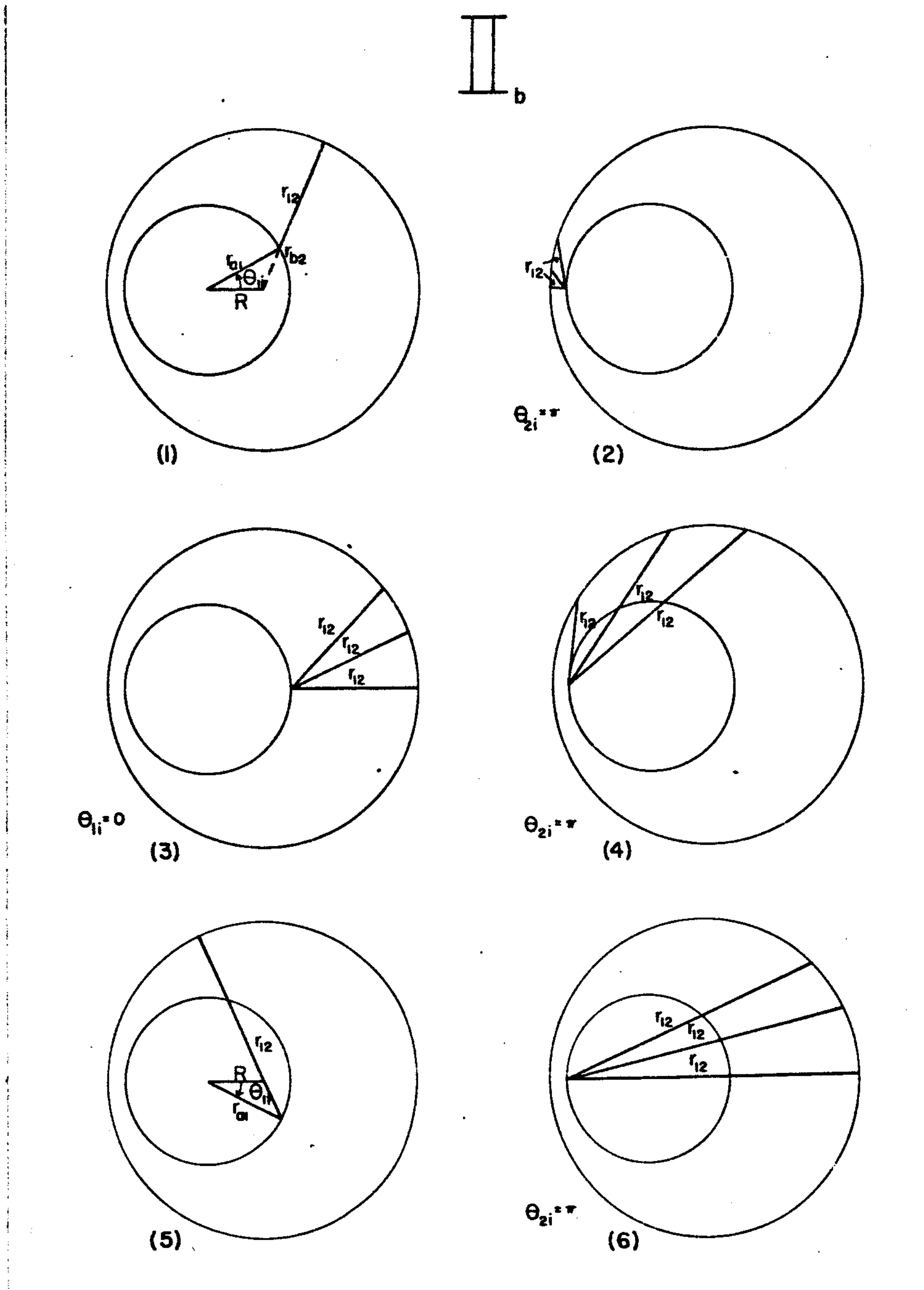

Fig. 8. The Limiting Angles θ_{1i} and θ_{2i} for Region II_b. Subfigures (1) and (2) refer to the Secondary Region $II_b(1)$: (3) and (4) refer to $II_b(2)$; and (5) and (6) refer to $II_b(3)$.

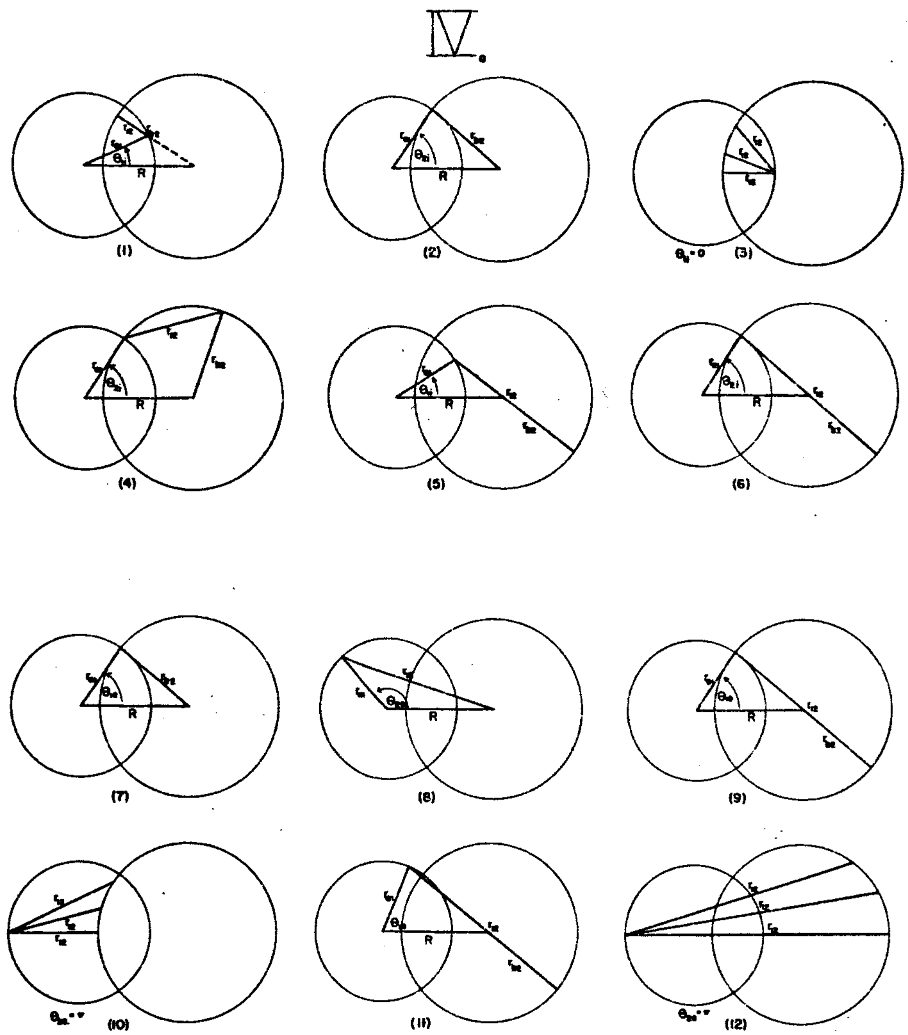

Fig. 9. The Limiting Angles θ_{1i}, θ_{2i}, θ_{1e} and θ_{2e} for Region IV_a. Subfigures (1) and (2) refer to the Secondary Region $IV_a(1)$(interior); (3) and (4) refer to $IV_a(2)$(interior); (5) and (6) refer to $IV_a(3)$ (interior): (7) and (8) refer to $IV_a(1)$ (exterior); (9) and (10) refer to $IV_a(2)$(exterior); and (11) and (12) refer to $IV_a(3)$(exterior).

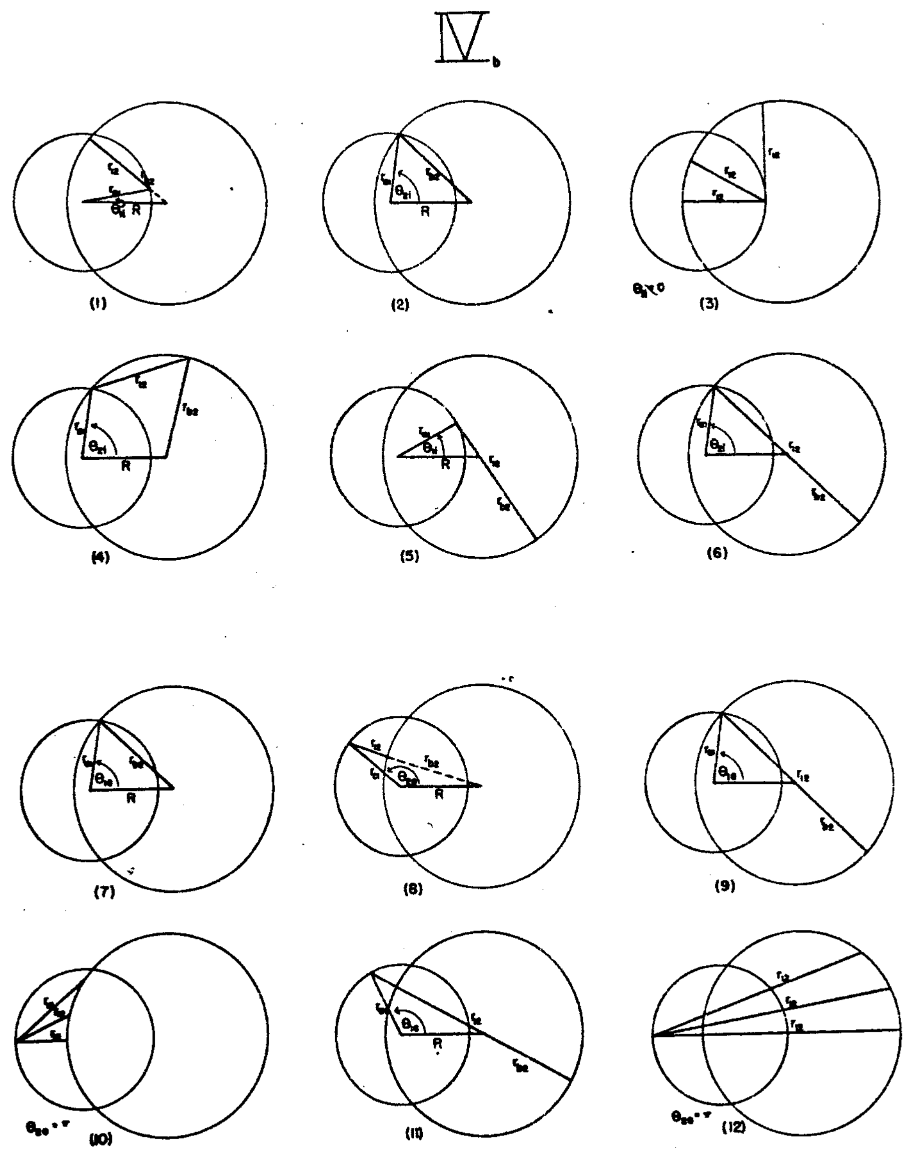

Fig. 10 The Limiting Angles θ_{1i}, θ_{2i}, θ_{1e} and θ_{2e} for Region IV_b. Subfigures (1) and (2) refer to the Secondary Region $IV_b(1)$(interior); (3) and (4) refer to $IV_b(2)$ (interior); (5) and (6) refer to $IV_b(3)$ (interior); (7) and (8) refer to $IV_b(1)$ (exterior); (9) and (10) refer to $IV_b(2)$(exterior); and (11) and (12) refer to $IV_b(3)$(exterior).

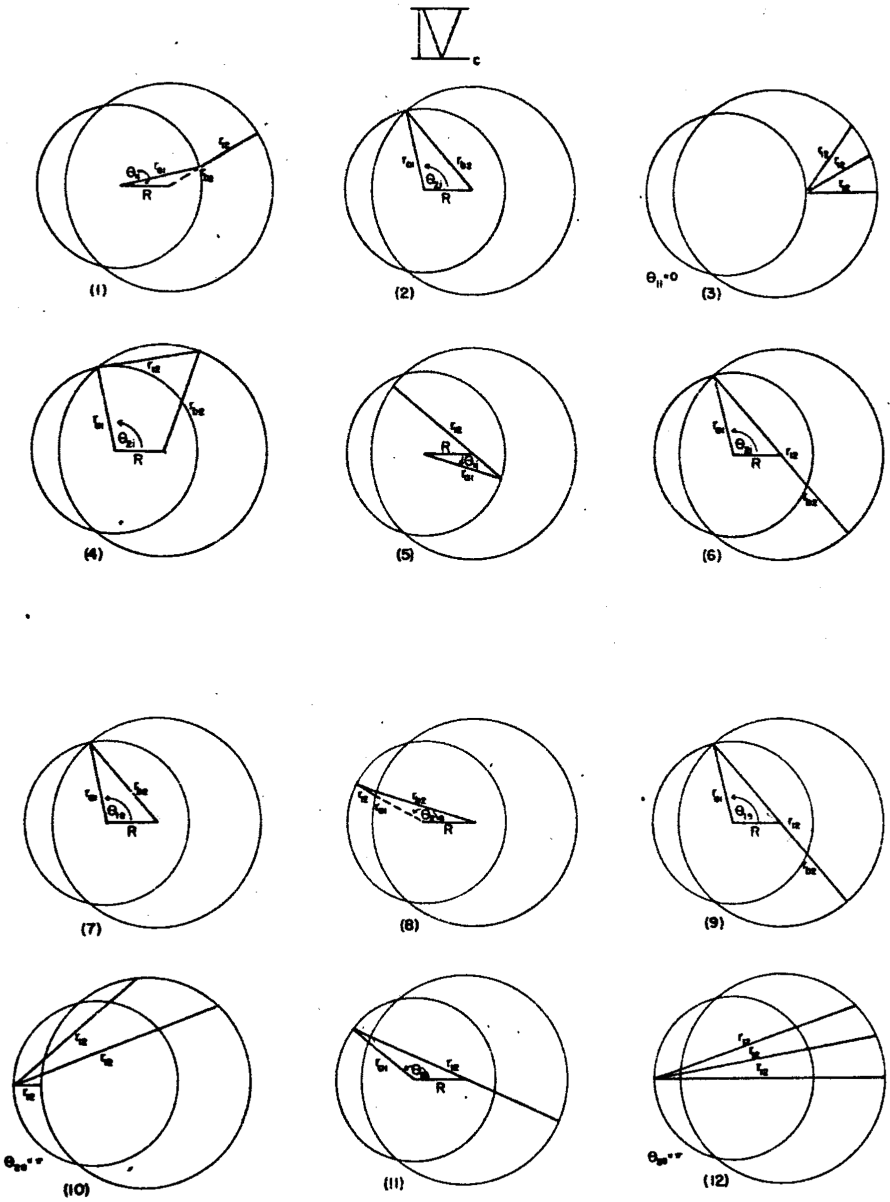

Fig. 11. The Limiting Angles θ_{1i}, θ_{2i} , θ_{1e} and θ_{2e} for Region IV_c. Subfigures (1) and (2) refer to the Secondary Region IV_c(1)(interior); (3) and (4) refer to IV_c(2)(interior); (5) and (6) refer to IV_c (3) (interior); (7) and (8) refer to IV_c (1)(exterior); (9) and (10) refer to IV_c(2) (exterior); and (11) and (12) refer to IV_c(3) (exterior).

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9. I. Prigogine, <u>Molecular Theory of Solutions</u>, (North Holland Publishing Co., Amsterdam, 1957), p. 267. Prigogine expanded r_{12}^{-m} in terms of Gegenbauer polynomials and then reexpanded in terms of spherical harmonics.

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11. Since ${}_2K'(0,0)_Y = 4$ (see Footnote 12), it follows from Eq. (40b) of Sack's third paper[10] that $\langle \delta(\underline{r}_1 - \underline{r}_2)\rangle_{IV} = -16 (\pi r_{a1} r_{b2} R)^{-1}$. Since the bipolar angle average of the delta function must be positive, it appears that Sack's Eq. (40b) must contain a typographical error. In the other master regions, we agree with Sack: $\langle \delta(\underline{r}_1 - \underline{r}_2)\rangle = 0$.

12. In Sack's notation[10]: I = S_3 , II = S_1 , III = S_2 , and IV = S_o. The coefficient $(r_{12}^{\,n}|0,0;0,0)$ corresponds to $l_1 = l_2 = l_3 = 0$ so that $\Lambda = \lambda_i = 0$. It is easy to show that the constant factor ${}_2K'(0,0)_Y = 4$.

Figure Captions

Fig. 1. Two-particle, Two-Center Coordinates

Fig. 2. Division of r_{a1}-r_{b2} Plane into Twelve Primary Regions

Fig. 3. Critical distances and configurations within primary regions which determine the Secondary Regions. The circles show why we call region I non-overlapping, IV_a slightly overlapping, IV_b and IV_c greatly overlapping, and II enclosing.

Fig. 4. Division of $r_{a1} - r_{b2}$ Plane into Four Master Regions.

Fig. 5. Area swept out on circle "b" from a point on circle "a" with θ_{a1}, r_{a1}, r_{b2}, and R held constant and r_{12} lying in the range r_{12} to $r_{12}+\delta r_{12}$.

Fig. 6. The Limiting Angles θ_{1e} and θ_{2e} for Region I_a. Subfigures (1) and (2) refer to Secondary Region $I_a(1)$; (3) and (4) refer to $I_a(2)$; and (5) and (6) to $I_a(3)$.

Fig. 7. The Limiting Angles θ_{1i} and θ_{2i} for Region II_a. Subfigures (1) and (2) refer to the Secondary Region $II_a(1)$; (3) and (4) refer to $II_a(2)$; and (5) and (6) refer to $II_a(3)$.

Fig. 8. The Limiting Angles θ_{1i} and θ_{2i} for Region II_b. Subfigures (1) and (2) refer to the Secondary Region $II_b(1)$: (3) and (4) refer to $II_b(2)$; and (5) and (6) refer to $II_b(3)$.

Fig. 9. The Limiting Angles θ_{1i}, θ_{2i}, θ_{1e} and θ_{2e} for Region IV_a. Subfigures (1) and (2) refer to the Secondary Region IV_a (1)(interior); (3) and (4) refer to $IV_a(2)$(interior); (5) and (6) refer to $IV_a(3)$ (interior); (7) and (8) refer to $IV_a(1)$ (exterior); (9) and (10) refer to $IV_a(2)$ (exterior); and (11) and (12) refer to $IV_a(3)$ (exterior).

Fig. 10. The Limiting Angles θ_{1i}, θ_{2i}, θ_{1e} and θ_{2e} for Region IV_b. Subfigures (1) and (2) refer to the Secondary Region $IV_b(1)$ (interior); (3) and (4) refer to $IV_b(2)$ (interior); (5) and (6) refer to $IV_b(3)$ (interior); (7) and (8) refer to $IV_b(1)$ (exterior); (9) and (10) refer to $IV_b(2)$ (exterior); and (11) and (12) refer to $IV_b(3)$ (exterior).

Figure Captions (continued)

Fig.11. The Limiting Angles θ_{1i}, θ_{2i}, θ_{1e} and θ_{2e} for Region IV_c. Subfigures (1) and (2) refer to the Secondary Region IV_c(1) (interior): (3) and (4) refer to IV_c(2) (interior); (5) and (6) refer to IV_c(3) (interior); (7) and (8) refer to IV_c(1) (exterior); (9) and (10) refer to IV_c(2) (exterior); and (11) and (12) refer to IV_c(3) (exterior).